

# PATENT SPECIFICATION

NO DRAWINGS

1,141,165



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No. 17010/66

Date of Application and filing Complete  
Specification: 19 April, 1966.

Application made in Germany (No. A50154ivd/39c) on  
31 August, 1965.

Complete Specification Published: 29 January, 1969.

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Index at Acceptance:—C3 P (8A, 8D2A, 8D2B2, 8D5, 8D8, 8K8, 8K9, 8K11, 8P1B, 8P1C,  
8P1D, 8P1E4, 8P1F, 8P4A, 8P5, 8P6D, 8P6X).

Int. Cl.:—C 08 f 1/86.

## COMPLETE SPECIFICATION

### Process for the Manufacture of Acrylic Films

We, FIRMA ASCHAFFENBURGER ZELLS-  
TOFFWERKE AKTIENGESELLSCHAFT, a joint  
stock company organised under the laws  
of Germany, of Redenfelden/Obb. Germany,  
5 do hereby declare the invention, for which  
we pray that a patent may be granted to  
us and the method by which it is to be  
performed, to be particularly described in  
and by the following statement:

10 The present invention relates to a process  
for the production of acrylic polymers, with  
the special purpose of manufacturing plastic  
films.

15 The usual method for manufacturing  
plastic films consists in the extrusion of  
polymers or precipitation from polymeric  
solutions and subsequent stretching of the  
film formed. By means of the so-called bulk  
polymerization, polymers with a parti-  
20 cularly smooth and non-porous surface are  
obtained.

25 It is known that acrylic and methacrylic  
acid ester polymers are—depending on their  
chemical composition—hard, elastic or  
plastic materials. It is further known that  
the elasticity of polymers can be improved  
by so-called internal plasticizers, e.g. by  
30 copolymerization of methacrylic acid methyl  
ester with esters of acrylic acid having  
short-chain alkyl groups ( $C_1$  to  $C_{12}$ ). While  
the elasticity of products thus obtained is  
sufficient for inherently stable materials of  
a thickness of approximately 0.5 mm and  
more, it is insufficient for the manufacturing  
35 of films which have to withstand a consider-  
ably higher elastic strain.

Furthermore, it is known that the poly-  
merization of methacrylic acid methyl ester  
and its homologues, as well as the poly-  
40 merization of acrylic acid alkyl esters, in  
the presence of phosphoric acid anhydride  
and alcohols result in flameproof films, the  
phosphoric acid anhydride and alcohol con-

densation product acting as an external  
plasticizer which does not take part in the 45  
polymerization reaction.

It is further known that by two-dimen-  
sional or three-dimensional cross-linking the  
swelling properties and the solubility of  
such products can be reduced ad libitum, 50  
whereby the dimensional stability under  
heat and the hardness of the polymers are  
increased.

According to the present invention there  
is provided a process for manufacturing 55  
acrylic films, wherein a methacrylic acid  
alkyl ester having 1 to 4 carbon atoms in  
the alkyl group (A), in an amount between  
50% and 90%, is reacted by free radical  
bulk polymerization, with an acrylic acid 60  
ester (B) in an amount between 5% and  
40% and with 5% to 45% of an ester of a  
polyethoxylated product containing at least  
one acrylic or methacrylic acid ester-group  
and optionally an ester group derived from 65  
another aliphatic or aromatic mono- or di-  
carboxylic acid (C), the percentages being  
by weight and based on the total weight of  
the monomers, and the reaction being  
carried out between two shaping members 70  
to produce a film.

It is to be understood that the acrylic ester  
(B) does not include the esters of a poly-  
ethoxylated product as defined for (C).

The acrylic ester (B) may be an alkyl ( $C_1$  75  
to  $C_{12}$ ), alkoxyalkyl, hydroxyalkyl, haloalkyl,  
epoxyalkyl, aryl, arylalkyl, or alkylaryl  
acrylate. A preferred material is an acrylic  
n-butyl ester present in an amount of be-  
tween 10% and 20% by weight. 80

The acrylic monomer (A) is preferably  
methacrylic acid methyl ester.

Component (C) is preferably present in  
an amount of 15% to 25% and may be a  
dimethacrylic or diacrylic acid ester of a 85  
polyalkylene glycol. Instead of the dimeth-

[Price 4s. 6d.]

acrylic or diacrylic acid esters of polyalkylene glycols, it is possible to use the following mixed esters; mono-methacrylic or -acrylic acid -monopropionic or -butyric or -stearic acid ester of polyalkylene glycols, or bis-(polyalkyleneglycol mono-methacrylate or acrylate) esters of maleic, phthalic, terephthalic, fumaric, or itaconic acid:

e.g.  $\text{H}_2\text{C}:\text{C}(\text{CH}_3)\text{CO}-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n-\text{CO}.\text{CH}:\text{CH}.\text{CO}-(\text{O}.\text{CH}_2\text{CH}_2\text{O})_n-\text{O}-\text{CO}.\text{C}(\text{CH}_3):\text{CH}_3$  is "bis (poly-alkylene glycol mono-methacrylate) maleic acid ester".

It is advantageous to use the mixed esters of the poly-ethoxylated compounds derived from both saturated and unsaturated aliphatic or aromatic mono- and/or dicarboxylic acids.

The polymerization is carried out in the usual manner by moulding, preferably between glass plates or inert metal foils or plastic foils, with addition of the usual free radical catalysts, and, if necessary, of accelerators or activators with or without heat supply,

The process may include the step of prepolymerizing two or more of the monomer reactants.

The polymer films produced can easily be stripped from the supports, e.g. plates or foils, particularly in the case when component (C) is a methacrylic or acrylic acid ester of a polyethoxylated alkylphenol.

The acrylic polymer films produced in this way show, depending on their composition, good properties in respect of tensile strength, bursting strength, workability and transparency.

The invention is illustrated by the following Examples, where all parts and percentages referred to are by weight, unless otherwise stated.

#### EXAMPLE I

69.7 parts methacrylic acid methyl ester, 45 10.0 parts acrylic acid n-butyl ester and 20.0 parts of the dimethacrylic acid ester of polyethyleneglycol (M.Wt 600) were prepolymerized to syrup consistency with 0.03 parts azodiisobutyronitrile. After cooling 0.3 parts crosslinking agent (the dimethacrylic acid ester of triethylene glycol) and polymerization catalyst comprising 2.0 parts permaleic acid tertiary butyl ester (paste—50% plasticizer), 1.6 parts lauryl mercaptan, 55 1.0 part activator solution, (40% benzyl dimethyl laurylammoniumchloride, 0.217%  $\text{CuCl}_2$  and balance ethyl alcohol) were added.

This mixture was poured after de-aeration 60 on to a flat inert supporting film, covered with a second film, and after adjusting the thickness by pressing with a roll, it was polymerized at 50°C to a flexible tenacious colourless film.

#### EXAMPLE II

57.5 parts methacrylic acid methyl ester, 20.0 parts acrylic acid n-butyl ester, 20.0 parts mixed methacrylic acid — propionic acid ester of polyethylene glycol (M.Wt 600) and 2.0 parts methacrylic acid ester of a 70 polyethoxylated nonyl phenol were prepolymerized to syrup consistency with 0.03 parts azodiisobutyronitrile. After cooling, 0.5 parts crosslinking agent (the dimethacrylic acid ester of triethylene glycol) and the 75 polymerization catalyst consisting of 0.5 parts permaleic acid tertiary butyl ester (paste—50% plasticizer) and 0.5 parts activator (1 molar proportion of  $\text{ZnO}$  and 2 molar proportions of thioglycolic acid 2-80 ethyl-hexyl ester) were added. The mixture was de-aerated by vacuum, pressed with a roll between supporting films and polymerised at 55°C. A highly elastic colourless film with high water vapour permeability 85 was obtained.

#### WHAT WE CLAIM IS:—

1. Process for manufacturing acrylic films, wherein a methacrylic acid alkyl ester 90 having 1 to 4 carbon atoms in the alkyl group (A), in an amount between 50% and 90%, is reacted by free radical bulk polymerization, with an acrylic acid ester (B) in an amount between 5% and 40%, and 95 with 5% to 45% of an ester of a polyethoxylated product containing at least one acrylic or methacrylic acid ester group and optionally an ester group derived from another aliphatic or aromatic mono- or di-carboxylic acid (C), the percentages being by weight and based on the total weight of the monomers, and the reaction being carried out between two shaping members to produce a film.

2. Process according to claim 1, wherein the monomer (A) is methacrylic acid methyl ester.

3. Process according to claim 1, wherein the acrylic acid ester (B) is an alkyl ( $\text{C}_1$  to 110  $\text{C}_n$ ), alkoxyalkyl, hydroxyalkyl, haloalkyl, epoxyalkyl, aryl, arylalkyl, or alkylaryl acrylate.

4. Process according to any preceding claim, wherein the acrylic acid ester (B) is 115 acrylic acid n-butyl ester and is present in an amount of between 10% and 20% by weight.

5. Process according to any preceding claim, wherein the ester (C) is a dimethacrylic acid ester or monomethacrylic acid-monopropionic ester of polyethylene glycol and is present in an amount of between 15% and 25% by weight.

6. Process as claimed in any preceding 125 claim, which includes the step of prepolymerizing two or more of the monomer reactants.

7. Process for manufacturing acrylic

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films as claimed in claim 1 and substantially as hereinbefore described with reference to either of the Examples.

8. Acrylic films whenever prepared or produced by a process claimed in any of the preceding claims.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd, Berwick-upon-Tweed, 1969.  
Published at the Patent Office, 25 Southampton Buildings, London, W.C.2 from which copies may be obtained.